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Coating compositions and adhesives, their use and
5 processes for their preparation

The present invention relates to novel coating compositions and adhesives, to their use and to processes for preparing them.

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The coating materials that are known nowadays, such as clearcoats or topcoats, surfacers and primers, or compositions for the underbody protection of motor vehicles, are based on binders which need to have a

15 large number of different properties in order for the required coating properties to be obtained. Such coating systems are known, for example, from German Patents DE 44 07 415, DE 44 07 409 or DE 43 10 414. The disadvantage of all these coating materials is that it

20 is not possible to increase the solids contents ad infinitum. With these systems therefore, the possibilities for reducing the solvent emission is confined within narrow limits. Similar comments apply to adhesives.

25

The object of the present invention is therefore to provide coating compositions or adhesives which, compared to the coating compositions known to date, have a higher solids content and which allow low-emission formulations. In the case of the coating compositions the intention is in particular to remove the disadvantages associated with the use of customary, known reactive diluents, such as the incipient dissolution of other coating films on application and

30 35 the reduction in thermal and light stability. Furthermore, it is intended that the novel coating compositions shall combine otherwise unchanged basic properties with improved scratch resistance and good reflow characteristics.

This object is achieved in accordance with the invention by means of the novel coating composition or adhesive comprising

- 5 a) at least one binder,
b) at least one crosslinker, and
c) at least one branched, cyclic and/or acyclic C₉-C₁₆-alkane which is functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group.

In the light of the prior art it was not foreseeable

that these compounds could be derived by means of the branched, cyclic and/or acyclic C₉-C₁₆-alkanes c), to be used in accordance with the invention, which are functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group, since the concern was that these compounds too would have the disadvantages of other reactive diluents.

In the text below the branched, cyclic and/or acyclic C₉-C₁₆-alkanes c) to be used in accordance with the invention, which are functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group, are referred to for the sake of brevity as "functionalized alkanes c)".

The functionalized alkanes c) which are essential to the invention are derived from branched, cyclic or acyclic alkanes having 9 to 16 carbon atoms forming in each case the parent structure.

Examples of suitable alkanes of this kind having 9 carbon atoms are 2-methyloctane, 4-methyloctane, 2,3-dimethylheptane, 3,4-dimethylheptane, 2,6-dimethyl-

heptane, 3,5-dimethylheptane, 2-methyl-4-ethylhexane and isopropylcyclohexane.

Examples of suitable alkanes of this type having 10
5 carbon atoms are 4-ethyloctane, 2,3,4,5-tetra-
methylhexane, 2,3-diethylhexane or 1-methyl-2-n-
propylcyclohexane.

Examples of suitable alkanes of this type having 11
10 carbon atoms are 2,4,5,6-tetramethylheptane and
3-methyl-6-ethyloctane.

Examples of suitable alkanes of this type having 12
carbon atoms are 4-methyl-7-ethylnonane, 4,5-diethyl-
15 octane, 1'-ethylbutylcyclohexane, 3,5-diethyloctane and
2,4-diethyloctane.

Examples of suitable alkanes of this type having 13
carbon atoms are 3,4-dimethyl-5-ethylnonane and 4,6-
20 dimethyl-5-ethylnonane.

An example of a suitable alkane of this type having 14
carbon atoms is 3,4-dimethyl-7-ethyldecane.

25 Examples of suitable alkanes of this type having 15
carbon atoms are 3,6-diethylundecane and 3,6-dimethyl-
9-ethylundecane.

30 Examples of suitable alkanes of this type having 16
carbon atoms are 3,7-diethyldodecane and 4-ethyl-6-isopropylundecane.

Of these parent structures, the alkanes having 10 to 14
and especially 12 carbon atoms are particularly
35 advantageous and are therefore used with preference. Of
these, in turn, the octane derivatives are especially
advantageous.

For the present invention it is essential that the functionalized alkanes c) which are derived from these branched, cyclic or acyclic alkanes as parent structures are liquid at room temperature. Therefore it
5 is possible to use either individual liquid functionalized alkanes c) or liquid mixtures of these compounds. This is the case in particular when using functionalized alkanes c) which, owing to their high number of carbon atoms in the alkane parent structure,
10 are solid in the form of individual compounds. The person skilled in the art is therefore able to select the appropriate functionalized alkanes c) in a simple manner.

15 16 17
functionalized alkanes c) have a boiling point of more than 200, preferably 220 and, in particular, 240°C. In addition, they should have a low evaporation rate.

20 For the adhesives and coating compositions of the invention it is advantageous if the functionalized alkanes c) are acyclic.

25 The functionalized alkanes c) have primary and/or secondary hydroxyl and/or thiol groups. For the adhesives and coating compositions of the invention it is advantageous if primary and secondary groups of this type are present in one compound.

30 The functionalized alkanes c) are, accordingly, polyols, polythiols or polyol-polythiols c), but especially polyols c). These compounds can be used individually or together in the form of mixtures. Particular advantages arise if the polyols c) are diols
35 and/or triols, but especially diols. They are therefore used with very particular preference.

Especially advantageous adhesives and coating compositions of the invention are obtained if the

polyols c) are positionally isomeric dialkyloctanediois, especially diethyloctanediois. Outstanding results are obtained with 2,4-diethyl-1,5-octanediol.

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The above-described functionalized alkanes c) are compounds which are known per se and can be prepared by means of customary and known synthesis methods of organic chemistry such as the base-catalyzed aldol 10 condensation, or are obtained as byproducts of large-scale chemical syntheses such as the preparation of 2-ethylhexanol.

In general, the functionalized alkanes c) are present 15 in the adhesives and coating compositions of the invention in an amount from 0.5 to 25% by weight, based on the overall amount of the constituents a) + c). Although they may be present therein in larger amounts, this is an advantageous range within which the 20 advantages of the invention are obtained in a sure and reliable manner. Within this range, that from 1 to 20% by weight is of particular advantage, because the adhesives and coating compositions of the invention which contain this amount of functionalized alkanes c) 25 have a particularly advantageous profile of properties. Meanwhile, very particular advantages result from the use of 2 to 15% by weight of functionalized alkanes c).

The adhesives and coating compositions of the invention 30 comprise at least one binder a) as a further essential constituent. This binder a) generally comprises an oligomeric or polymeric resin which has functional groups that react with the crosslinker b) to form three-dimensional networks. These functional groups can 35 be any customary and known functional groups. However, it is of advantage in accordance with the invention if the binders a) have functional groups of the same type as the functionalized alkanes c). In this context,

hydroxyl groups are of very special advantage and are therefore used with very particular preference.

Suitable candidates for the hydroxy-functional binder
5 a) or for the mixture of hydroxy-functional binders a)
are preferably hydroxy-functional polyacrylates,
polyesters, polyurethanes, acrylicized polyurethanes,
acrylicized polyesters, polylactones, polycarbonates,
polyethers and/or (meth)acrylatediols a). Hydroxy-
10 functional binders a) are known to the person skilled
in the art, and numerous suitable examples are
available on the market.

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Preference is given to the use of polyacrylates,

~~polyacrylates and/or polyesters a).~~

Polyacrylate resins a) have OH numbers of from 40 to
240, preferably from 60 to 210 and, with very
20 particular preference, from 100 to 200, acid numbers of
from 0 to 35, preferably from 0 to 23, and with very
particular preference, from 3.9 to 15.5, glass
transition temperatures of from -35 to +70°C,
preferably from -20 to +40°C and, with very particular
25 preference, from -10 to +15°C, and number-average
molecular weights of from 1500 to 30,000, preferably
from 1500 to 15,000 and, with very particular
preference, from 1500 to 5000.

30 The glass transition temperature of the polyacrylate
resins a) is determined by the nature and amount of the
monomers employed. The selection of the monomers can be
performed by the person skilled in the art with the aid
of the following formula, by which it is possible to
35 calculate approximately the glass transition
temperatures of polyacrylate resins a):

$n=x$

$$1/Tg = \sum_{n=1}^x w_n/Tg_n ; \sum_n w_n = 1$$

$n=1$

Tg = glass transition temperature of the polyacrylate resin

5 w_n = proportion by weight of the nth monomer

Tg_n = glass transition temperature of the homopolymer of the nth monomer

x = number of different monomers

10 Measures to control the molecular weight (e.g., selection of corresponding polymerization initiators, use of chain transfer agents, etc.) are part of the technical knowledge of the person skilled in the art and need not be elucidated further here.

15

As the hydroxy-functional binder component a) it is also possible, for example, to employ polyacrylate resins which can be prepared by subjecting (a1) from 10 to 92, preferably from 20 to 60% by weight of an alkyl

20 or cycloalkyl acrylate or of an alkyl or cycloalkyl methacrylate having from 1 to 18, preferably 4 to 13 carbon atoms in the alkyl or cycloalkyl radical, or mixtures of such monomers, (a2) from 8 to 60, preferably from 12.5 to 38.5% by weight of a

25 hydroxyalkyl acrylate or of a hydroxyalkyl methacrylate having from 2 to 4 carbon atoms in the hydroxyalkyl radical, or mixtures of such monomers, (a3) from 0.0 to 5.0, preferably from 0.7 to 3.0% by weight of acrylic acid or methacrylic acid, or mixtures of these

30 monomers, and (a4) from 0 to 50, preferably from 0 to 30% by weight of ethylenically unsaturated monomers which are different from but copolymerizable with (a1), (a2) and (a3), or mixtures of such monomers, to polymerization to give polyacrylate resins having

35 hydroxyl numbers of from 40 to 240, preferably from 60 to 150, acid numbers of from 0 to 35, preferably from 5

to 20, glass transition temperatures of from -35 to +70 degrees C, preferably from -20 to +40 degrees C, and number-average molecular weights of from 1500 to 30,000, preferably from 1500 to 15,000 (determined by

5 gel permeation chromatography with polystyrene standard). Examples of components (a1) are methyl, ethyl, propyl, n-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl and 2-ethylhexyl acrylate and methacrylate and also cyclohexyl acrylate and 10 cyclohexyl methacrylate. Examples of components (a2) are hydroxyethyl, hydroxypropyl and hydroxybutyl acrylate and methacrylate. Examples of components (a4) are vinylaromatic compounds, such as styrene,

15 ring-substituted diethylstyrenes, isopropylstyrene, butylstyrenes and methoxystyrenes; vinyl ethers, such as ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether and isobutyl vinyl ether and vinyl esters, such as vinyl acetate, vinyl 20 propionate, vinyl butyrate, vinyl pivalate and the vinyl ester of 2-methyl-2-ethylheptanoic acid. The hydroxyl number and acid number of the polyacrylate resins can easily be controlled by the person skilled in the art by way of the amount of components (a2) and 25 (a3) employed, respectively.

Further suitable polyacrylate components a) are the hydroxy-functional compounds specified in European Patent Application EP 0 767 185 and in US Patents 5 480 30 943, 5 475 073 and 5 534 598.

Examples of further hydroxy-functional binder components a) which are employed are polyacrylate resins which are obtainable by subjecting (a1) from 10 35 to 51% by weight, preferably from 25 to 41% by weight, of 4-hydroxy-n-butyl acrylate or 4-hydroxy-n-butyl methacrylate or a mixture of 4-hydroxy-n-butyl acrylate and 4-hydroxy-n-butyl methacrylate, preferably 4-hydroxy-n-butyl acrylate, (a2) from 0 to 36% by weight,

preferably from 0.1 to 20% by weight, of a hydroxyl-containing ester of acrylic acid or of a hydroxyl-containing ester of methacrylic acid which is different from (a1), or of a mixture of such monomers, (a3) from 5 28 to 85% by weight, preferably from 40 to 70% by weight, of an aliphatic or cycloaliphatic ester of methacrylic acid having at least 4 carbon atoms in the alcohol residue and being different from (a1) and (a2), or of a mixture of such monomers, (a4) from 0 to 3% by 10 weight, preferably from 0.1 to 2% by weight, of an ethylenically unsaturated carboxylic acid or of a mixture of ethylenically unsaturated carboxylic acids, and (a5) from 0 to 20% by weight, preferably from 5 to 15% by weight, of an unsaturated monomer which is 15 different from (a1), (a2), (a3) and (a4), or of a mixture of such monomers, to polymerization to give a polyacrylate resin a) having a hydroxyl number of from 60 to 200, preferably from 100 to 160, an acid number of from 0 to 35, preferably from 0 to 25, and a number-average molecular weight of from 1500 to 10,000, 20 preferably from 2500 to 5000, the sum of the parts by weight of components (a1) to (a5) always being 100% and the composition of component (a3) being chosen such that polymerization of component (a3) alone gives a 25 polymethacrylate resin having a glass transition temperature of from +10 to +100 degrees C, preferably from +20 to +60 degrees C. Examples of component (a2) are hydroxyalkyl esters of acrylic acid, such as hydroxyethyl acrylate and hydroxypropyl acrylate, and 30 hydroxylalkyl esters of methacrylic acid, such as hydroxyethyl methacrylate and hydroxypropyl methacrylate, the choice being made such that polymerization of component (a2) alone gives a polyacrylate resin having a glass transition 35 temperature of from 0 to +80 degrees C, preferably from +20 to +60 degrees C. Examples of component (a3) are aliphatic esters of methacrylic acid having 4 to 20 carbon atoms in the alcohol residue, such as n-butyl, isobutyl, tert-butyl, 2-ethylhexyl, stearyl and lauryl

methacrylate, and cycloaliphatic esters of methacrylic acid, such as cyclohexyl methacrylate. As component (a4) it is preferred to employ acrylic acid and/or methacrylic acid. Examples of component (a5) are 5 vinylaromatic hydrocarbons, such as styrene, alpha-alkylstyrene and vinyltoluene, amides of acrylic and methacrylic acid, such as methacrylamide and acrylamide, nitriles of acrylic and methacrylic acid, vinyl ethers and vinyl esters. It is preferred as 10 component (a5) to employ vinylaromatic hydrocarbons, especially styrene. The composition of component (a5) should preferably be chosen such that polymerization of component (a5) alone gives a polymer having a glass transition temperature of from +70 to +120 degrees C,

of these polyacrylate resins a) can be carried out in accordance with general and well-known polymerization techniques (see e.g. Houben-Weyl, Methoden der organischen Chemie, 4th edition, Volume 14/1, pages 24 20 to 255 (1961)). They are preferably prepared by means of solution polymerization. In this case, usually an organic solvent or solvent mixture is introduced as initial charge and heated to boiling. Then the monomer mixture to be polymerized, along with one or more 25 polymerization initiators, is added continuously to this organic solvent or solvent mixture. Polymerization takes place at temperatures between 100 and 200 degrees C, preferably between 130 and 180 degrees C. The polymerization initiators employed are preferably 30 initiators which form free radicals. The nature and amount of initiator are customarily chosen such that the supply of free radicals during the feed phase at the polymerization temperature is extremely constant. Examples of initiators which can be employed are 35 dialkyl peroxides, such as di-tert-butyl peroxide and dicumyl peroxide, hydroperoxides, such as cumene hydroperoxide and tert-butyl hydroperoxide, per esters, such as tert-butyl perbenzoate, tert-butyl perpivalate, tert-butyl per-3,5,5-trimethylhexanoate and tert-butyl

per-2-ethylhexanoate, and bisazo compounds, such as azobisisobutyronitrile. The polymerization conditions (reaction temperature, feed time of the monomer mixture, nature and amount of the organic solvents and

5 polymerization initiators, possible use of molecular weight regulators, e.g., mercaptans, thioglycolic esters and chlorinated hydrocarbons) are selected such that the polyacrylate resins a) have a number-average molecular weight as indicated (determined by gel 10 permeation chromatography using polystyrene as calibrating substance). The acid number can be adjusted by the person skilled in the art using appropriate amounts of component (a4). Similar comments apply to the adjustment of the hydroxyl number. It can be 15 controlled by way of the amount of component (a1) and (a2) employed.

In addition, it is possible to use commercial polyacrylates which are sold under the brand name of Joncrys®, such as Joncrys® SCX912 and 922.5.

20 Suitable polyester resins and alkyd resins a) can be prepared by reacting (a1) a cycloaliphatic or aliphatic polycarboxylic acid or a mixture of such polycarboxylic acids, (a2) an aliphatic or cycloaliphatic polyol 25 having more than two hydroxyl groups in the molecule or a mixture of such polyols, (a3) an aliphatic or cycloaliphatic diol or a mixture of such diols, and (a4) an aliphatic linear or branched saturated monocarboxylic acid or a mixture of such monocarboxylic acids in a molar ratio of (a1):(b1):(c1):(d1) = 1.0:0.2-30 1.3:0.0-1.1:0.0-1.4, preferably 1.0:0.5-1.2:0.0-0.6:0.2-0.9 to give a polyester resin or alkyd resin, respectively. Examples of the constituent (a1) are hexahydrophthalic acid, 1,4-cyclohexanedicarboxylic 35 acid, endomethylenetetrahydphthalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebamic acid. Examples of the constituent (a2) are pentaerythritol, trimethylolpropane, trimethylolethane

and glycerol. Examples of the constituent (a3) are ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, 2-methyl-2-propyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-propanediol, 2,2,4-trimethyl-1,5-pentanediol, 2,2,5-trimethyl-1,6-hexanediol, neopentyl glycol hydroxypivalate and dimethylolcyclohexane. Examples of the constituent (a4) are 2-ethylhexanoic acid, lauric acid, isoctanoic acid, isononanoic acid and monocarboxylic acid mixtures obtained from coconut oil or palm kernel oil.

The preparation of hydroxyl-bearing polyester resins and/or alkyd resins ^{a)} is described, for example, in Ullmanns Encyklopädie der technischen Chemie, 3rd

Berlin 1963, pages 80 to 89 and pages 99 to 105, and in the following books: Résines Alkydes-Polyesters by J. Bourry, Paris Dunod 1952, Alkyd Resins by C.R. Martens, Reinhold Publishing Corporation, New York 1961 and Alkyd Resins Technology by T.C. Patton, Interscience Publishers, 1962.

Other suitable binders, moreover, are those based on polyurethanes ^{a)}. Urethane (meth)acrylates ^{a)} are well known to the person skilled in the art and need not therefore be elucidated further. Examples of suitable polyurethane resins ^{a)} are the resins described in patents EP 0 708 788, DE 44 01 544 or DE 195 34 361.

Through the partial replacement of the binders and binder mixtures ^{a)} described above by the functionalized alkanes ^{c)} to be used in accordance with the invention it is possible, surprisingly, to achieve relatively high solids contents without substantial disadvantages in terms of the profile of properties of the coatings or adhesives. Thus with markedly higher solids contents of the coating compositions of the invention and with comparable acid resistance of the coatings it has been possible to achieve scratch

resistance and film hardness values which in accordance with the prior art were hitherto possible only at lower solids contents. In accordance with the invention, therefore, it is possible in particular to obtain a 5 higher reflow potential and, by virtue of the higher solids content, a reduction in the solvent emission.

- In addition to the above-described binders a), the adhesives and coating compositions of the invention 10 also comprise other constituents, which are customary in the prior art. In this context it is possible to formulate the coating compositions of the invention as one-component or else multi-component systems. Such systems differ essentially in the nature of the 15 crosslinker b) that is employed. In both cases, suitable crosslinkers b) are all those which react with hydroxyl groups under the curing conditions. Examples of suitable crosslinkers b) are amino resins, siloxane-functional compounds or resins, anhydride-functional 20 compounds or resins, blocked and non-blocked polyisocyanates and/or alkoxy carbonylaminotriazines, but especially blocked polyisocyanates and/or tris(alkoxy carbonyl amino) triazines b).
- 25 In accordance with the invention, blocked isocyanates b) or a mixture of blocked polyisocyanates b) can be employed both in one-component and two-component systems.
- 30 The blocked isocyanates b) which can be employed are preferably designed such that they include both isocyanate groups blocked by a blocking agent (Z1) and isocyanate groups blocked by a blocking agent (Z2), the blocking agent (Z1) being a dialkyl malonate or a 35 mixture of dialkyl malonates, the blocking agent (Z2) being a blocking agent other than (Z1) which contains active methylene groups, or being an oxime or a mixture of these blocking agents, and the ratio of equivalents between the isocyanate groups blocked with (Z1) and the

isocyanate groups blocked with (Z2) being between 1.0:1.0 and 9.0:1.0, preferably between 8.0:2.0 and 6.0:4.0 and, with particular preference, between 7.5:2.5 and 6.5:3.5.

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In addition, dimethylpyrazole and/or substituted triazoles are suitable as blocking agents.

The blocked isocyanate b) is preferably prepared as follows:

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A polyisocyanate or a mixture of polyisocyanates is reacted conventionally with a mixture of the blocking agents (Z1) and (Z2), the mixture of blocking agents (Z1) and (Z2) comprising the blocking agents (Z1) and

9.0:1.0, preferably between 8.0:2.0 and 6.0:4.0 and, with particular preference, between 7.5:2.5 and 6.5:3.5.

20 The polyisocyanate or the mixture of polyisocyanates can be reacted with the mixture of the blocking agents (Z1) and (Z2) to such an extent that isocyanate groups can no longer be detected. In practice, this may require the use of very large excesses of blocking 25 agents and/or very long reaction times.

It has been found that coating materials having good properties are obtained even if at least 50, preferably at least 70 percent of the isocyanate groups of the 30 polyisocyanate or of the mixture of polyisocyanates are reacted with the mixture of the blocking agents (Z1) and (Z2) and if the remaining isocyanate groups are reacted with a hydroxyl-containing compound or with a mixture of hydroxyl-containing compounds. Hydroxyl-containing compounds employed are preferably low 35 molecular mass aliphatic or cycloaliphatic polyols, such as neopentyl glycol, dimethylolcyclohexane, ethylene glycol, diethylene glycol, propylene glycol, 2-methyl-2-propyl-1,3-propanediol, 2-ethyl-2-butyl-1,3-

isophorone diisocyanate with 0.3-0.5 equivalent of a low molecular mass polyol having a molecular weight from 62 to 500, preferably from 104 to 240, in particular a triol, such as trimethylolpropane, for example.

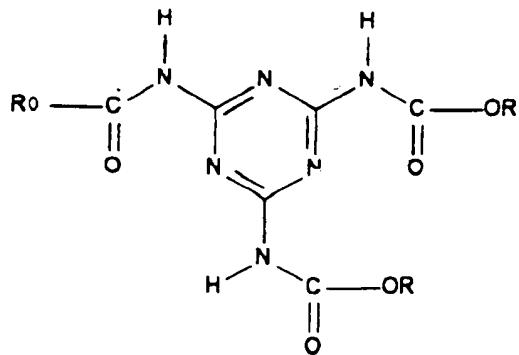
Dialkyl malonates or a mixture of dialkyl malonates are or is employed as blocking agent (Z1). Examples of dialkyl malonates which can be employed are those 10 having 1 to 6 carbon atoms in each of the alkyl radicals, examples being dimethyl malonate and diethyl malonate, and with diethyl malonate being employed with preference. Blocking agents different from (Z1) containing active methylene groups, and also oximes and 15 mixtures of these blocking agents, are employed as blocking agent (Z2). Examples of blocking agents which can be employed as blocking agent (Z2) are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl or dodecyl acetoacetate, acetone oxime, 20 methyl ethyl ketoxime, acetyl acetone, formaldoxime, acetaldoxime benzophenoxime, acetoxime and diisobutylketoxime. As blocking agent (Z2) it is preferred to employ an alkyl acetoacetate having 1 to 6 carbon atoms in the alkyl radical, or a mixture of such alkyl 25 acetoacetates, or a ketoxime or a mixture of ketoximes. Particular preference is given to the use of ethyl acetoacetate or methyl ethyl ketoxime as blocking agent (Z2).
30 Other crosslinkers b) which can be employed are tris(alkoxycarbonylamino)triazines b) of the formula

propanediol, 2,2,4-trimethyl-1,5-pentanediol and 2,2,5-trimethyl-1,6-hexanediol or the hydroxyl-containing binder (a) which can be employed as constituent (a).

- 5 A suitable blocked polyisocyanate b) is also obtainable by mixing blocked polyisocyanates with the blocking agent (Z1) or (Z2) in a ratio such that in the resultant mixture the ratio of equivalents between the isocyanate groups blocked with (Z1) and the isocyanate 10 groups blocked with (Z2) lies between 1.0:1.0 and 9.0:1.0, preferably between 8.0:2.0 and 6.0:4.0 and, with particular preference, between 7.5:2.5 and 6.5:3.5.
- ..

principle to employ any of the polyisocyanates that can be employed in the paints field. It is preferred, however, to employ polyisocyanates whose isocyanate groups are attached to aliphatic or cycloaliphatic 20 radicals. Examples of such polyisocyanates are hexamethylene diisocyanate, isophorone diisocyanate, trimethylhexamethylene diisocyanate, dicyclohexylmethane diisocyanate, 1,3-bis(2-isocyanatoprop-2-yl)-benzene (TMXDI) and 1,4- and 1,3-bis(iso-cyanato-25 methyl)cycloalkanes such as 1,4- and 1,3-bis-(isocyanatomethyl)cyclohexane and also adducts of these polyisocyanates with polyols, especially low molecular mass polyols, such as trimethylolpropane, and isocyanurate- and/or biuret-functional polyisocyanates 30 derived from these polyisocyanates.

Polyisocyanates employed with particular preference are hexamethylene diisocyanate and isophorone diisocyanate, isocyanurate- or biuret-functional polyisocyanates 35 which are derived from these diisocyanates and preferably contain more than two isocyanate groups in the molecule, and also products of reaction of hexamethylene diisocyanate and isophorone diisocyanate or of a mixture of hexamethylene diisocyanate and



in which R = methyl and/or other alkyl groups, especially butyl groups. Derivatives of said compounds
5 can also be employed. As crosslinkers b) it is preferred to employ tris(alkoxycarbonyl-amino)triazines as described in US Patent 5 084 541.

The coating compositions of the invention can also be
10 multi-component systems, preferably two-component systems. In this case, the coating composition has a second component which comprises as crosslinker b) at least one non-blocked di- and/or polyisocyanate b) which is dissolved, if desired, in one or more organic
15 solvents. In addition, however, blocked polyisocyanate or a mixture of blocked polyisocyanates b) may also be present in the second component.

The free polyisocyanate constituent b) which can be
20 employed comprises any desired organic polyisocyanate having free isocyanate groups attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic structures. Preference is given to the use of polyisocyanates having 2 to 5 isocyanate groups per molecule and
25 viscosities of from 100 to 2000 mPa.s (at 23 degrees C). If desired, small amounts of organic solvent, preferably from 1 to 25% by weight, based on pure polyisocyanate, may be added to the polyisocyanates in order to ease their incorporation and, if desired, to
30 reduce the viscosity of the polyisocyanate to a level which is within the abovementioned ranges.

- Examples of solvents suitable as additives for the polyisocyanates are ethoxyethyl propionate, butyl acetate and the like. Examples of suitable isocyanates 5 are described, for example, in Methoden der organischen Chemie, Houben-Weyl, Volume 14/2, 4th edition, Georg Thieme Verlag, Stuttgart 1963, pages 61 to 70, and by W. Siefken, Liebigs Ann. Chem. 562, 75 to 136.
- 10 Suitable, for example, are polyisocyanates and/or isocyanate-functional polyurethane prepolymers b) which can be prepared by reacting polyols with an excess of polyisocyanates and which are preferably of low viscosity. It is also possible to employ polyisocyanates which contain biuret groups and/or allophanate groups and/or urethane groups and/or urea groups and/or uretdione groups. Polyisocyanates having urethane groups, for example, are obtained by reacting some of the isocyanate groups 20 with polyols, such as trimethylolpropane and glycerol, for example. Preferably employed are aliphatic or cycloaliphatic polyisocyanates, especially hexamethylene diisocyanate, dimerized and trimerized hexamethylene diisocyanate, isophorone diisocyanate, 25 2-isocyanatopropylcyclohexyl isocyanate, dicyclohexylmethane 2,4'-diisocyanate or dicyclohexylmethane 4,4'-diisocyanate, or mixtures of these polyisocyanates.
- 30 Very particular preference is given to using mixtures of polyisocyanates which have uretdione and/or isocyanurate groups and/or allophanate groups and which are based on hexamethylene diisocyanate, such mixtures being obtained by catalytic oligomerization of hexamethylene diisocyanate using suitable catalysts. 35 The polyisocyanate constituent b) can, moreover, consist of any desired mixtures of the free polyisocyanates exemplified above.

In particular, the coating composition of the invention may also include UV absorbers and free-radical scavengers. It may also include catalysts for crosslinking. Particularly suitable for this purpose are organometallic compounds, preferably organotin and/or organobismuth compounds. Tertiary amines may also be suitable. The coating composition may, furthermore, include rheological agents and other coatings auxiliaries. It is of course also possible to employ pigments of any kind, examples being color pigments such as azo pigments, phthalocyanine pigments, carbonyl pigments, dioxazine pigments, titanium dioxide, pigmentary carbon black, iron oxides and oxides of chromium and/or cobalt, or effect pigments, such as metal flake pigments, especially aluminum flake pigments, and pearlescent pigments.

In addition, the coating composition of the invention can, if desired, comprise customary auxiliaries and/or additives as well, examples being slip additives, polymerization inhibitors, matting agents, defoamers, leveling agents and film-forming auxiliaries, e.g., cellulose derivatives, or other additives commonly employed in basecoats. These customary auxiliaries and/or additives are commonly employed in an amount of up to 15% by weight, preferably from 2 to 9% by weight, based on the weight of the coating composition without pigments and without fillers.

The coating composition of the invention is prepared in a procedure in accordance with the invention by substituting from 0.5 to 25% by weight, preferably from 1 to 20 and, in particular, from 2 to 15% by weight, of the binder a) of a coating composition or of an adhesive by at least one functionalized alkane c) to be used in accordance with the invention. For this purpose, the customary methods, such as the combination of the individual constituents and their mixing with stirring, are employed. The preparation of the coating composition consisting of two or more components takes

place likewise by means of stirring or dispersing, using the apparatus commonly employed; for example, by means of dissolvers or the like or by means of two-component metering and mixing units that are likewise 5 customarily employed. The individual components are stored separately until their appropriate use.

The coating composition or adhesive of the invention is preferably formulated as a nonaqueous solution or 10 dispersion (i.e., containing organic solvents). For this purpose it is possible to use the organic solvents that are customary in the production of coatings or adhesives.

particular for producing coated moldings or composites which consist of or comprise films, glass, wood, paper and/or metal by applying the coating composition to the corresponding moldings and curing the resultant 20 coating.

The coating composition of the invention is preferably used to produce one- or multi-coat paint systems and, with particular preference, to produce topcoats. 25 Alternatively, it may be intended for the production of a clearcoat that is to be applied over a basecoat film, for example a clearcoat of a multi-coat paint system produced by the wet-on-wet technique. Furthermore, it can be used as a primer, surfacer or underbody 30 protection. It is of course possible for the plastics or other substrates to be coated directly with the clearcoat or topcoat.

The coating compositions can be employed both for the 35 OEM finishing and for the refinishing of car bodies. They are preferably employed, however, in the OEM finishing sector.

The adhesive of the invention is used to produce bonded composites which consist of or comprise films, plastics, glass, wood, paper and/or metal by applying the adhesive to the surface(s) that are to be bonded of 5 a film or of a plastic-, glass-, wood-, paper- and/or metal-containing or -comprising molding and/or to the surface(s) of the part which is to be bonded to it and, if desired, is initially cured, after which the respective surfaces to be bonded are brought into 10 contact and, subsequently, the adhesive is fully cured.

Application is generally performed with the aid of customary methods, for example by spraying, knife coating, dipping or brushing.

15 The adhesives or coating compositions of the invention are preferably cured at temperatures from room temperature up to 180°C. Particularly preferred temperatures are those between 60 and 180°C. In 20 specific embodiments of the coating compositions of the invention it is also possible to employ lower curing temperatures of from 60 to 160°C.

Moldings and composites which consist of or comprise 25 films, plastics, glass, wood, paper and/or metal and include at least one layer of the cured binder and/or at least one layer of the cured adhesive possess distinct advantages over customary moldings and composites in terms of thermal stability, light 30 stability, scratch resistance and weathering stability.

The invention is described in more detail below with reference to the examples:

Example

Table 1:

5 Composition of the inventive (B, C) and of the conventional (A) two-component system

Constituents	Composition	A	B	C
(Parts by weight)				
<u>Component I^{j,k}</u>				
Isocyanate hardener ^a	33	37.0	45.7	
<u>Component II^{j,k}</u>				
	82.87	75	67.3	
Diethyloctanediol [*]		4.5	9.0	
TIN 384 ^c	1.2	1.2	1.2	
TIN 292 ^d	1.0	1.0	1.0	
DBTL ^e	0.004	0.004	0.004	
Worlee ^R -ADD315 ^f	0.096	0.096	0.096	
ZN 73-1280 ^g	1.5	1.5	1.5	
Butylglycol acetate	3.93	3.93	3.93	
Xylene	0.2	4.67	4.67	
Solvent naphtha			3.2	
GB ester ^h	4.5	4.5	4.5	
Ethoxypropyl acetate	2.0	2.0	2.0	
Butanol	1.6	1.6	1.6	
Total	100	100	100	

a) = 80% solution of Desmodur N3390 (polyisocyanate

10 based on hexamethylene diisocyanate, from Bayer) in butyl acetate and solvent naphtha (crosslinker b)

b) = Customary and known acrylate resin made from

15 styrene, n-butyl methacrylate, t-butyl acrylate, hydroxypropyl methacrylate and acrylic acid, as acrylate resin (diluted to 53% solid content with a mixture of methoxypropyl acetate, butyl glycol acetate and butyl acetate) (binder a)

i) = Mixture of different positionally isomeric diethyloctanediois c) obtained from the industrial preparation of 2-ethylhexanol; gas chromatogram on 5 silylated sample:

	Retention time (min)	Area%
	23.01	0.5
10	23.14	0.8
	23.67	32.1
	23.71	14.4
	23.82	28.1
	23.85	18.6
15	28.53	0.6
	30.55	1.0

c) = Commercial light stabilizer Tinuvin 384^R from Ciba Specialty Chemical Inc.

20 d) = Commercial light stabilizer Tinuvin 292^R from Ciba Specialty Chemical Inc.

e) = Dibutyltin dilaurate

25 f) = Commercial leveling additive from Worlee, Lauenburg

30 g) = 5% solution of a polyether-substituted polydimethylsiloxane in xylene

h) = Glycolic acid butyl ester from Wacker

j = Viscosity of component II (DIN 4 cup s at 23°C):

Composition (parts by weight)	A	B	C
	29 s	22 s	20.5 s
k = Solids content of components I and II (1h, 125°C) at processing viscosity:	-	53.6%	61.0%

Performance tests:

5

1. BART test (chemical resistance)

The BART (BASE ACID RESISTANCE TEST) is used to determine the resistance of coated

10 acids, alkalis and water drops. During the test, the coating, after baking in a gradient oven, is exposed to further temperature loads (30 minutes at 40°C, 50°C, 60°C and 70°C). Beforehand, the test substances (sulfuric acid 1%, 10%, 36%; sulfurous acid 6%;
15 hydrochloric acid 10%; sodium hydroxide 5%; deionized water - 1,2,3 or 4 drops are applied in a defined manner using a metering pipette. After the substances have been allowed to act, they are removed under running water and the damage is assessed visually after
20 24 h in accordance with a predetermined scale:

Rating Appearance

0 No defect

1 Slight marking

25 2 Marking/matting/no softening

3 Marking/matting/change in shade/softening

4 Cracks/incipient through-etching

5 Clearcoat removed

30 Each individual mark (spot) is evaluated and the result for each coating is noted in appropriate form (e.g., total ratings for one temperature). The results are given in Table 1.

Table 1: Result of performance testing by the BART test

	Composition A				Composition B				Composition C			
Temperature (°C)	40	50	60	70	40	50	60	70	40	50	60	70
H ₂ SO ₄ 1%	0	0	0	4.5	0	0	0	4.5	0	0	0	4
H ₂ SO ₄ 10%	0	0	0	4.5	0	0	0	4.5	0	0	0	4
H ₂ SO ₄ 36%	0	0	0	4.5	0	0	0.5	4.5	0	0	0	4
HCl 10%	0	0	0	2	0	0	0	1.5	0	0	0	2
H ₂ SO ₃ 5%	0	0	0	4	0	0	0	4	0	0	0	4.5
NaOH 5%	0	0	0	1	0	0	0	1	0	0	0	1
Deionized water 1	0	0	1.5	1	0	0	0	1.5	0	0	0	2
Deionized water 2	0	0	0	2	0	0	0	2	0	0	0	1
Deionized water 3	0	0	0	2	0	0	0.5	1.5	0	0	1	2
Deionized water 4	0	0	0	1	0	0	0.5	1.5	0	0	1	1
Total acid	0	0	0	20.5	0	0	0.5	20	0	0	0	19.5
Total water	0	0	1.5	6	0	0	1	6	0	0	2	6

2. Sand test (scratch resistance)

5

In the sand test, the coated surface is exposed to sand (20 g of quartz silver sand 1.5-2.0 mm). The sand is placed in a PE beaker (with its base cut off planarly) which is secured firmly to the test panel. Using a motor drive, the panel with the beaker and the sand is set in oscillation. The movements of the loose sand results in damage to the coated surface (100 double strokes in 22 s). Following sand exposure, the test area is cleaned to remove abraded material, carefully wiped off under a jet of cold water, and then dried with compressed air. The gloss in accordance with DIN 67530 is measured before and after damaging, at 10 20°.

15

20 This test procedure tests the scratch resistance of coated surfaces (clearcoats and topcoats) against washing-brush scratches. The procedure is

a good imitation of the exposure of a coated surface in a wash unit.

The results of the test are given in Table 2.

5

Table 2: Results of the sand test

Gloss values^{a)}	A	B	C
Initial gloss	84	84	84
Residual gloss	53.5	55.6	56.8
Gloss after 2 h, 40°C	55.3	58.0	60.1
Gloss after 2 h, 60°C	57.1	63.3	68.2

10

The results of the BART test on the one hand, and of the sand test on the other, underline the fact that the two-component systems (B and C) of the invention are equal to the conventional two-component system (A) in 15 their high acid resistance but considerably exceeded in scratch resistance, especially in reflow behavior at elevated temperatures, and in the solids content.

Patent Claims

1. A coating composition or adhesive comprising
 - 5 a) at least one binder,
 - b) at least one crosslinker, and
 - c) at least one branched, cyclic and/or acyclic
10 C_9-C_{16} -alkane which is functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group.
- 15 2. The coating composition or adhesive as claimed in claim 1, wherein the functionalized alkane c) is liquid at room temperature.
- 20 3. The coating composition or adhesive as claimed in claim 1 or 2, wherein the functionalized alkane c) has a boiling point of more than 200°C.
- 25 4. The coating composition or adhesive as claimed in one of claims 1 to 3, wherein the functionalized alkane c) is acyclic.
- 30 5. The coating composition or adhesive as claimed in one of claims 1 to 4, wherein the functionalized alkane c) has primary and/or secondary, especially primary and secondary, hydroxyl and/or thiol groups.
- 35 6. The coating composition or adhesive as claimed in one of claims 1 to 5, wherein the functionalized alkane c) is a polyol c).
7. The coating composition or adhesive as claimed in claim 6, wherein the polyols c) are diols and/or triols c).

8. The coating composition or adhesive as claimed in
claim 7, wherein the polyols c) are positionally
isomeric dialkyloctanediools, especially diethyl-
octanediools.

5
9. The coating composition or adhesive as claimed in
claim 8, wherein the polyol c) consists of or
comprises 2,4-diethyl-1,5-octanediol.

10
10. The coating composition or adhesive as claimed in
one of claims 1 to 9, wherein the functionalized
alkane c) is present therein in an amount from 0.5
to 25, preferably from 1 to 20 and, in particular,

amount of the constituents a) + c).

20
11. The coating composition or adhesive as claimed in
one of claims 1 to 10, which comprises a multi-
component system in which at least the crosslinker
b) is stored separately from the other components
until its appropriate use.

25
12. The coating composition or adhesive as claimed in
claim 11, which comprises a two-component system
having a first component which comprises the
crosslinker b) and a second component which
comprises the binder a) and the functionalized
alkane c).

30
13. The coating composition or adhesive as claimed in
one of claims 1 to 10, which comprises a one-
component system which comprises the binder a),
the crosslinker b) and the functionalized alkane
c).

35
14. The use of the coating composition or adhesive as
claimed in one of claims 1 to 13 to coat or bond
plastic surfaces, including film surfaces, wood

surfaces, glass surfaces, paper surfaces or metal surfaces.

15. The use of the coating composition as claimed in
5 one of claims 1 to 13 in automotive OEM finishing
and automotive refinishing as a clearcoat,
topcoat, surfacer, primer and/or underbody
protection.

- 10 16. The use of C₉-C₁₆-alkanes c) which are
functionalized with at least two hydroxyl or thiol
groups or with at least one hydroxyl group and at
least one thiol group to produce coating
compositions and adhesives.
15

17. The use as claimed in claim 16, wherein the
functionalized alkane c) is liquid at room
temperature.
20

18. The use as claimed in claim 16 or 17, wherein the
functionalized alkane c) has a boiling point of
more than 200°C.
25

19. The use as claimed in claims 16 to 18, wherein the
functionalized alkane c) is acyclic.
30

20. The use as claimed in one of claims 16 to 19,
wherein the functionalized alkane c) has primary
and/or secondary, especially primary and
secondary, hydroxyl and/or thiol groups.
35

21. The use as claimed in one of claims 16 to 20,
wherein the functionalized alkane c) is a polyol
c).
35

22. The use as claimed in claim 21, wherein the
polyols c) are diols and/or triols c).

23. The use as claimed in claim 22, wherein the polyols c) are positionally isomeric dialkyloctanediools, especially diethyloctanediools.

5 24. The use as claimed in claim 23, wherein the polyol c) consists of or comprises 2,4-diethyl-1,5-octanediol.

10 25. A process for producing coating compositions or adhesives by mixing their constituents, which comprises at least mixing

a) at least one binder,

15 b) at least one crosslinker, and

20 c) at least one branched, cyclic and/or acyclic C₉-C₁₆-alkane which is functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group,

with one another.

25 26. The process as claimed in claim 25, wherein the functionalized alkane c) is liquid at room temperature.

30 27. The process as claimed in claim 25 or 26, wherein the functionalized alkane c) has a boiling point of more than 200°C.

35 28. The process as claimed in one of claims 25 to 27, wherein the functionalized alkane c) is acyclic.

29. The process as claimed in one of claims 25 to 28, wherein the functionalized alkane c) has primary and/or secondary, especially primary and secondary, hydroxyl and/or thiol groups.

30. The process as claimed in claim 29, wherein the functionalized alkane c) is a polyol c).

5 31. The process as claimed in claim 30, wherein the polyols c) are diols and/or triols c).

10 32. The process as claimed in claim 31, wherein the polyols c) are positionally isomeric dialkyl-
octanediols, especially diethyloctanediols.

15 33. The process as claimed in claim 32, wherein the polyol c) consists of or comprises 2,4-diethyl-
1,5-octanediol.

34. A process for producing coated moldings or composites which consist of or comprise films, glass, wood, paper and/or metal by applying a coating composition to the corresponding moldings
20 and curing the resultant coating, which comprises using the coating composition as claimed in one of claims 1 to 13.

25 35. A process for producing bonded composites which consist of or comprise films, plastics, glass, wood, paper and/or metal by applying an adhesive to the surface(s) that are to be bonded of a film or of a plastic-, glass-, wood-, paper- and/or metal-containing or -comprising molding and/or to
30 the surface(s) of the part which is to be bonded to it and, if desired, is initially cured, after which the respective surfaces to be bonded are brought into contact and, subsequently, the adhesive is fully cured, which comprises using the adhesive as claimed in one of claims 1 to 13.

36. A molding or composite which consists of or comprises film, plastic, glass, wood, paper and/or metal and has at least one layer of the cured

binder as claimed in one of claims 1 to 13 and/or at least one layer of the cured adhesive as claimed in one of claims 1 to 13.



Abstract

Coating composition or adhesive comprising

- a) at least one binder,
- b) at least one crosslinker, and
- c) at least one branched, cyclic and/or acyclic C₉-C₁₆-alkane which is functionalized with at least two hydroxyl or thiol groups or with at least one hydroxyl and at least one thiol group.

